Sometimes chemo- and bio-catalysis are in open competition (C_1-oxidation and -dehydrogenation, C_2-oxidation), in other oxidations (e.g. glycolic splitting) the choice is limited.

In carboxy-alkylation direct methods (carboxymethylation) as well as indirect routes (e.g. via the nitrile) are applied. This will be exemplified for inulin and model compounds.

Finally, anhydrides may be used to attach carboxylate groups to carbohydrates. As an example the addition of D-glucamine to DTPA-bisanhydride will be obtained. The Gd(III)-complex of the tricarboxylate obtained may serve as MRI contrast agent.

Quantification of Arabinose in Pectic Polysaccharides by FT-IR spectroscopy

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The sequential extraction of the cell wall material (CWM) of olive and orange pulps and its subsequent fractionation by ethanol precipitation and anion-exchange chromatography gave a wide range of fractions rich in cell wall polysaccharides. The fractions rich in pectic polysaccharides are characterized by the presence of uronic acid, rhamnose, arabinose and galactose monosaccharides released by acid hydrolysis. The FT-IR spectra in the 1200–850 cm^{-1} region allows the prediction of the amount of arabinose, as a molar percentage of the total sugars, in the pectic polysaccharide samples of the two distinct fruits. Regression models for the arabinose content were constructed. In order to highlight the selective wavenumbers for the determination of the arabinose present in the pectic polysaccharides, a selection of variables was made based on a mathematical method that uses the signal to noise ratio and a PLSI regression procedure. For the olive samples, the relevant wavenumbers, in decreasing order of importance, are: 1111, 1107, 1049, 1069, 1065, 1045, 1103, 1053, 1115, 1146, 1061, 1014, 1057 cm^{-1}; for the orange samples, the relevant wavenumbers are: 1049, 1065, 1115, 1045, 1061, 1053, 1041, 1111, 1057 cm^{-1}. For both systems, the absorbances in the regions 1115–1111 cm^{-1} and 1065–1045 cm^{-1} were found to be important for the prediction of the content of arabinose in the pectic samples. This study reports the potential of these regions to predict the amount of arabinose of pectic origin, as a quick evaluation, from different sources.

Recent Advances in the Synthesis of Carbohydrate Mimics

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C-disaccharides are close analogues of disaccharides in which the interglycosidic oxygen atom has been replaced by a methylene group. The major part of the lecture will deal with the detailed presentation of a flexible synthetic strategy based on a 8 or 9 *endo-trig* radical cyclisation reaction from two monosaccharides temporarily connected through a chemical tether. It will delineate the scope of the procedure, analyze variations on the theme, and describe some biological aspects.

Two novel reactions will also be described:

1. The one step stereoselective conversion of a sugar derivative into a highly substituted cyclopentane derivative.
2. The one step stereoselective conversion of a sugar derivative into a highly substituted cyclohexane derivative.

Sialyl Lewis^x and Synthetic Analogues Thereof as New Antiinflammatory Drugs

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Leukocyte influx from blood vessels into the surrounding tissue can be a beneficial response of the body to control infections and injuries. Excessive leukocyte influx, however, may result in an acute or chronic reaction as observed in reperfusion injuries or respiratory diseases.

The first step in the cascade of events which finally leads to the recruitment of leukocytes is their adhesion to the endothelial cell surface. It has been shown that an inducible set of calcium dependent adhesion molecules, the so-called selectins, are involved in this initial step. A possible strategy for preventing the negative effects of an excessive leukocyte influx is the inhibition of the leukocyte/selectin interactions. Therefore, intense efforts have been directed at defining the ligand of the three known selectins. It was found that the selectin ligands have a common epitope, which is the Sialyl Lewis^x tetrasaccharide.

Sialyl Lewis^x has served as a lead structure in our search for simplified and more potent selectin antagonists. Our strategy may be summarized as follows:

1. Elucidation of the structure/activity relationship of the lead structure (SAR study) and determination of its conformation bound to the selectin (bioactive conformation).
2. Development of molecular modeling tools for the rational design of new potential selectin antagonists.
3. Preparation of potential selectin antagonists by chemical and enzymatic synthesis.
4. Evaluation of the antagonists in appropriate *in vitro* assays (under static and flow conditions) and *in vivo* models (intravital microscopy, peritonitis).

Stereocommunication Through Glycosidic Linkages

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Glycosides are of paramount importance in chemistry and biology. They are ubiquitous in Nature and possess wide-ranging biological properties. Important low molecular weight glycosides include sucrose (a sweetening agent), digitoxin (a cardiotonic agent), streptomycin (an antibacterial agent) and adriamycin (an anticancer agent). Heightened by the discovery that glycoside domains of glyconjugates are involved in cell–cell, cell-bacterium and cell–virus interactions and the expectation that low molecular weight carbohydrate-related constructs may serve as drug-discovery leads, glycoside assembly is now a focus for synthetic chemists.

Glycosides with aglycones featuring stereogenic centres are traditionally assembled from sugars (in appropriately protected and anomerically activated forms) and aglycone alcohols (in protected forms if necessary). An alternative strategy, pursued in the author's group and the subject of this lecture, is the synthesis of glycosides with aglycone units that lack stereogenic centres and their subsequent elaboration into ones that possess them. Clearly, the success of such an approach depends critically upon the ability of the sugar units to